Far-infrared Spectra of Zinc Halide Complexes with Acetonitrile

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The infrared spectra of zinc halide complexes with acetonitrile, $ZnX_2 \cdot 2CH_3CN$ (X=Cl, Br, I), in the solid state were recorded in the region from 4000 to 96 cm^{-1}. The Zn–N stretching bands for the chloride and bromide were observed, at 210 and 212 cm^{-1} respectively, as composite bands of the A_1 and B_1 species. For the iodide, the Zn–N stretching band of the B_1 species was observed at 219 cm^{-1}, while the A_1 mode was coupled with the Zn–I stretching mode and was absorbed at 252 and 179 cm^{-1}. The N–Zn–N bending bands were observed at 163, 162, and 153 cm^{-1} and the Zn–N≡C bending bands, at 125, 128, and 132 cm^{-1}, for the chloride, bromide, and iodide respectively. The normal coordinate analysis was carried out by the use of the Urey-Bradley force field, and the Zn–N stretching force constant was obtained as 0.56 mdyn/Å. The force constant is much smaller than the corresponding ones in complexes containing nitrogen donors in the sp^3 and the sp^2 valency states.

It has been known that nitriles react with many metal halides to form σ-complexes by donating the lone-pair electron of the nitrogen atom.[1] The metal-nitrogen bonds in these complexes have generally been considered to be very weak, since the electron-donating ability of the nitrogen atoms in alkyl cyanides is weaker than that in amines or imines.[1] Many investigators have been interested in the strength of these coordinate bonds and have studied the infrared spectra of nitrile complexes with metal halides.[1,2] However, the number of studies in which metal-nitrogen stretching bands are observed is rather limited.

Infrared studies suggesting weak metal-nitrogen bonds have been published of the complexes of acetonitrile with $SnCl_4$,[1,3–5] $ZnCl_2$,[6] and NbX_5 and TaX_5 (X=Cl and Br).[7] In these studies, the metal-nitrogen stretching vibrations, ν_{MN}, have been assigned bands below 225 cm^{-1}.[8] Besides, the spectra of acetonitrile complexes with Pd(II), Pt(II), and Rh(II) halides have been reported to have no band above 200 cm^{-1} which can be assigned unambiguously to ν_{MN}.[9]

In contrast to the studies mentioned above, relatively high frequencies for ν_{MN}, 650—400 cm^{-1}, have been reported for such cyanide complexes as $M(CO)_3 \cdot 3CH_3CN$ (M=Cr, Mo, and W),[10] $BX_3 \cdot CH_3CN$ (X=Cl, Br, and F),[11,12] $AlCl_3ClCN$,[13] and cyanopyridine·$MClO_4$ (M=Cu(I), Ag(I), and Au(I)).[14] However, these high frequencies may be considered to reflect the M–N bonds strengthened by the high electron affinities of the metals characteristic of the IIIb-element halides and the metal carbonyls,[10,11] or by the increased electron-donating ability of the ligand nitrogen due to the contribution of an ionic resonance structure.[14]

Thus, ordinary metal halide-alkyl cyanide complexes appear to have very weak coordinate bonds and to give rise to M–N stretching bands around 200 cm^{-1}. Yet, our information on the coordination of this type cannot be said to be sufficient. Although the spectrum of $ZnCl_2 \cdot 2CH_3CN$ in a CH_3CN solution has already been studied,[6,15] the spectra associated with the skeletal modes have not been analysed completely. In addition, a band at 174 cm^{-1} assigned to the ν_{MN} by Evans and Lo[6] has not been observed in the Raman spectrum by Addison *et al.*[15] In order to get a clear vision of the M–N bonds in nitrile complexes, it was thought necessary to reexamine the far-infrared spectra of $ZnX_2 \cdot 2CH_3CN$.

Experimental

The complexes, $ZnX_2 \cdot 2CH_3CN$ (X=Cl, Br, and I), were prepared in the following manner. A saturated solution of 99% pure zinc halide in dry acetonitrile was prepared in a dry box filled with dry nitrogen gas. After the undissolved portions had then been filtered off, the solvent was evaporated moderately with an aspirator until white crystals appeared. The crystals were then collected and dried over P_2O_5 for two days. The complexes were considerably stable in dry air, but they were readily decomposed by atmospheric water vapour.

Found for the chloride: Cl, 31.79%. Calcd for $ZnCl_2 \cdot 2CH_3CN$: Cl, 32.47%. Found for the bromide: Br, 52.32%. Calcd for $ZnBr_2 \cdot 2CH_3CN$: Br, 52.01%. Found for the iodide: I, 63.16%. Calcd for $ZnI_2 \cdot 2CH_3CN$: I, 63.25%.

The infrared spectra ranging from 4000 to 400 cm^{-1} for liquid acetonitrile and the complexes were observed with KBr plates on a JASCO IR-G infrared spectrophotometer while the spectra in the low-frequency region from 500 to 96 cm^{-1} were observed with polyethylene plates on a Hitachi

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[1] R. A. Walton, *Quart. Rev.*, **19**, 126 (1965).

[2] See, *e.g.*, K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds, "John Wiley and Sons, Inc., New York (1963), p. 178.

[3] T. L. Brown and M. Kubota, *J. Amer. Chem. Soc.*, **83**, 4175 (1961).

[4] I. R. Beattie, G. P. McQuillan, L. Rule, and M. Webster, *J. Chem. Soc.*, **1963**, 1514.

[5] M. Farona and J. G. Grasselli, *Inorg. Chem.*, **6**, 1675 (1967).

[6] J. C. Evans and G. Y. S. Lo, *Spectrochim. Acta*, **21**, 1033 (1965).

[7] G. A. Ozin and R. A. Walton, *J. Chem. Soc.*, *A*, **1970**, 2236.

[8] Complexes, such as $NbCl_5 \cdot NCR$ and $TaCl_5 \cdot NCR$ (R=Cl and CH_3), have been studied by J. Maccordick and G. Kaufman, *J. Mol. Struct.*, **6**, 305 (1970). They have assigned the bands near 350 cm^{-1} to the M–N stretching vibrations. Therefore, there still remains a question on these assignments.

[9] R. A. Walton, *Spectrochim. Acta*, **21**, 1795 (1965); *Canad. J. Chem.*, **44**, 1480 (1966).

[10] M. F. Farona, J. G. Grasselli, and B. L. Ross, *Spectrochim. Acta*, **23A**, 1875 (1967).

[11] D. F. Schriver and B. Swanson, *Inorg. Chem.*, **10**, 1354 (1971).

[12] B. Swanson and D. F. Shriver, *ibid.*, **9**, 1406 (1970).

[13] K. Kawai and I. Kanesaka, *Spectrochim. Acta*, **25A**, 263 (1969).

[14] F. Farha and R. T. Iwamoto, *Inorg. Chem.*, **4**, 844 (1965).

[15] C. C. Addison, D. W. Amos, and D. Sutton, *J. Chem. Soc.*, *A*, **1968**, 2285; as for free acetonitrile, see also references therein.

TABLE 1. OBSERVED FREQUENCIES FOR THE LIQUID AND COMPLEXED ACETONITRILES (in cm^{-1}) AND THEIR ASSIGNMENTS[a)]

CH_3CN	$ZnCl_2\cdot 2CH_3CN$	$ZnBr_2\cdot 2CH_3CN$	$ZnI_2\cdot 2CH_3CN$	Assignment
	3240 vw	3252 vw	3251 vw	
		3218 vw	3200 vw	
3010 vs	2998 s	2995 s	2980 s	$a\nu$CH
2954 vs	2928 s	2925 s	2922 s	$s\nu$CH
2295 vs	2301 s	2316 s	2307 s	$s\delta CH_3+\nu CC$[b)]
2251 vs	2273 s	2285 s	2274 s	νCN
	2250 s	2251 s	2250 s	νCN[b)]
1440 vs, br	1442 s, br	1414 s, br	1414 s, br	$a\delta CH_3$
	1420 sh			
1375 vs	1376 s	1360 s, br	1356 s, br	$s\delta CH_3$
	1363 m			
1038 vs	1034 m, br	1024 s, br	1024 s, br	ρCH_3
	969 vw			
918 vs	924 m	943 s	940 s	νCC
	913 m			
	794 w	798 vw	786 vw	$2\cdot\delta$CCN
		773 vw	770 vw	$2\cdot\delta$CCN
	398 s	396 s	395 s	δCCN
365 s	389 s	386 s	385 s	δCCN
	380 s	379 s	378 s	δCCN

a) vs, very strong; s, strong; m, medium; w, weak; vw, very weak; ν, stretching; δ, bending; ρ,rocking.
b) Splitted bands due to Fermi resonance. See text.

TABLE 2. OBSERVED FREQUENCIES FOR $ZnX_2\cdot 2CH_3CN$ IN THE REGION BELOW 350 cm^{-1} AND THEIR ASSIGNMENT

$ZnCl_2\cdot$ $2CH_3CN$	$ZnBr_2\cdot$ $2CH_3CN$	$ZnI_2\cdot$ $2CH_3CN$	Assignment	
333			νZnCl	B_2
265			νZnCl	A_1
	261		νZnBr	A_1,B_2
		252	νZnI, νZnN	A_1
		219	νZnN	B_1
210	212		νZnN	A_1,B_1
		179	νZnN, νZnI	A_1
163	162	153	δNZnN	A_1
125	128	132	δZnNC	B_1,B_2

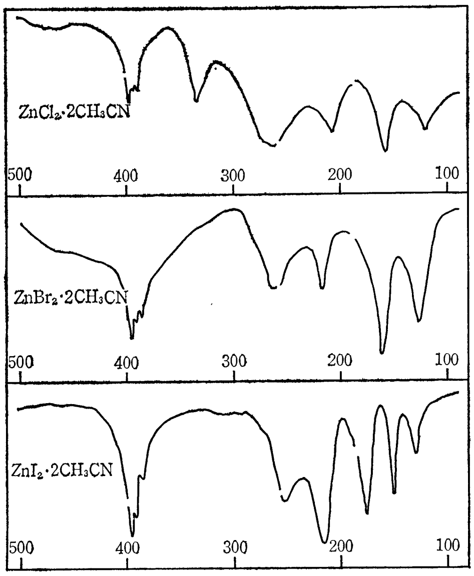

Fig. 1. Observed spectra of the complexes below 500 cm^{-1}.

FIS-21 far-infrared spectrophotometer. The mull method was empolyed for the solid samples. The observed frequencies associated with the ligand acetonitrile and the skeleton about the Zn atom are listed in Tables 1 and 2 respectively, while the spectra below 500 cm^{-1} are reproduced in Fig. 1.

Assignments

By considering the compositions of the samples and by referring to the structures of various zinc complexes previously determined,[16] it was assumed that these complexes have C_{2v} symmetry,[17] as other workers have done.[6,15] The infrared data for the complexes may be divided into intra-ligand and skeletal vibrational modes, which will be discussed separately.

Ligand Vibrations. The spectra of the complexed nitriles are very similar to one another and correspond very well with the spectra for uncomplexed acetonitrile except for the splittings of bands observed in the 2250, 1440, 1370, 920, and 380 cm^{-1} regions. If we consider that these splittings are caused by interaction between the two coordinated nitriles, the assignments of the observed bands to the intra-ligand vibrations can easily be made, as is shown in Table 1, by analogy with those for the free acetonitrile, which have been established

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[16] L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions," the Chemical Society, London (1965).

[17] According to the crystal structure analysis of $ZnCl_2\cdot 2CH_3CN$ carried out by I. V. Isakov and Z. V. Zvonkova, *Doklady Akad. Nauk U. S. S. R.*, **145**, 801 (1962), this molecule has a distorted tetrahedral structure about the Zn atom with a symmetry very close to C_{2v}. The structure parameters calculated from the given atomic coordinates are as follows: $\angle N\equiv C\text{–}CH_3$ 180°, $\angle Zn\text{–}N\equiv C$ 111°, $\angle ClZnCl$ 131°, $\angle NZnN$ 101°, Zn–N 1.95 Å, Zn–Cl 2.18 Å, C–C 1.51 Å, and C≡N 1.12 Å.

by several workers.[15,18,19]

The similarities between the frequencies for the free and complexed acetonitriles suggest that these complexes are formed by a weak σ-bonding through the lone-pair electrons. The band splittings observed over the entire spectra of the complexes, especially the splitting of the C–C≡N bending vibration into three bands, are consistent with the presumed symmetry.

The C–C stretching, ν_{CC}, and the C–C≡N bending frequencies were observed higher by as much as 4—22 cm^{-1} and 23—33 cm^{-1} respectively than those observed for the free ligand. These high frequency shifts may be caused by the coupling of the ligand vibrations with the skeletal mode of the complexes. This interpretation is supported by the normal coordinate analysis, which will be described in a later section. The lowest frequency band in the region of the C≡N stretching vibration, ν_{CN}, for the complexes was observed as low as the C≡N stretching frequency for the free nitrile. Despite the fact that a high frequency shift of ν_{CN} is generally characteristic of coordination through the lone-pair electrons on the nitrogen atoms of nitriles,[1,20] we assigned the lowest frequency band to one of the two expected ν_{CN} bands and the highest frequency band at about 2300 cm^{-1} to a combination band. These assignments are different from the assignments made by Evans and Lo,[6] but they are in accordance with those made by Addison *et al.* except for the assignment of the 2250 cm^{-1} band.[15] This apparently unshifted absorption can be interpreted as being due to the Fermi resonance occurring between the ν_{CN} and the combination band of the symmetric CH_3 deformation, $s\delta_{CH_3}$, and ν_{CC}, as was suggested in the previous studies of the spectra for the free nitrile.[15,18,21] The combination band, *e.g.*, the $1375+918=2293$ cm^{-1} band for the chloride, is located at a higher frequency than the ν_{CN} for the free molecule. When the ν_{CN} is shifted towards a higher frequency upon coordination and approaches more closely to the combination band, the two bands may suffer the effect of the Fermi resonance more strongly. As a result, the combination band may be raised, and the stretching band may be lowered in frequency, more in the complexed state than in the free state.

In addition to the assignment of the ν_{CN} band, the present interpretation is also somewhat different with regard to the splitting bands from those reported by previous workers, who studied the Raman and infrared spectra of a zinc chloride solution in CH_3CN.[6,15] They attributed the observed splitting bands to the fundamental vibrations belonging to the complexed and the free nitrile. However, similar splittings, as observed even in the spectra of the crystalline sample, indicate that the splittings observed in the solution spectra can not simply be ascribed to the vibrations of the sample in different states.

Skeletal Vibrations of Complexes. For the sekleton, L_2ZnX_2, of these complexes, fifteen normal modes of vibration, $4A_1+4A_2+3B_1+4B_2$, can be expected, including the librational modes of the ligands, L. Here, the subscripts 1 and 2 are used with reference to the LZnL plane. Among them, the two normal modes corresponding to methyl torsions, A_2+B_2, will not be observed in infrared spectra. It follows that a total of ten fundamental bands are to be assigned. In view of the similarity in the ligand vibrations, it may be considered that these complexes are in similar electronic states, and that the force constants of the internal potentials have similar magnitudes for all the complexes. Accordingly, each of the vibrational modes associated with the nitrogen atoms can be expected to absorb at nearly the same frequency, independent of the particular halogen atoms, while the other modes involving the halogen atoms absorb at different frequencies from one complex to another. For the chloride and bromide, one can easily identify two groups of bands; the first is a group of the zinc-halogen stretching vibrations, which decrease in frequency as the halogen atoms change from Cl to Br, while the second group consists of three bands, at about 210, 160, and 130 cm^{-1}, which are unaltered in position by the substituents. The observed bands at 333 and 265 cm^{-1} for the chloride undoubtedly belong to the first group and were assigned to the antisymmetric and symmetric Zn–Cl stretching modes, $a\nu_{ZnCl}$ and $s\nu_{ZnCl}$, respectively. The corresponding band for the bromide is that observed at about 260 cm^{-1}, where the two modes seem to overlap. The bands belonging to the second group are related to the coordinated nitrogen atoms. The band at 210 cm^{-1} may be assigned to the Zn–N stretching modes, ν_{ZnN}, which belong to the A_1 and B_1 species. Of the two bands at about 160 and 130 cm^{-1}, the higher was assigned to the N–Zn–N bending mode, δ_{NZnN}, and the lower, to the Zn–N≡C bending mode, δ_{ZnNC}, since the latter mode corresponds to the librational mode of the ligand and is expected to absorb at a lower frequency. There exist three infrared active librational modes of the ligands. Of them, the two modes of the B_1 and B_2 species were considered to overlap at about 130 cm^{-1}, and the A_1 mode, to lie below the observed frequency limit. These assignments were ascertained by the normal coordinate treatment, which will be described later. The present assignment of ν_{ZnN} differs from that made by Evans and Lo. We found no band at 174 cm^{-1}, but observed a band at 163 cm^{-1} (see Fig. 1). This band was then assigned to the δ_{NZnN}, as has been mentioned above.

The identification of bands for the iodide is not so clear as that for the chloride and bromide. However, the spectra of the iodide may be explained as follows. Generally, bands related to the Zn–I stretching modes, ν_{ZnI}, in various zinc iodide complexes are known to be observed at about 220 cm^{-1},[22,23] a frequency nearly equal to those assigned to ν_{ZnN} for the chloride and

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18) I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **18**, 514 (1962).

19) G. Graner, *C. R. Acad. Sci. Paris Ser., B*, **269**, 126 (1969).

20) K. F. Purcell and R. S. Drago, *J. Amer. Chem. Soc.*, **88**, 919 (1966).

21) K. Venkateswarhu and R. Thanalkshmir, *Indian J. Pure Appl. Phys.*, **1**, 64 (1963).

22) a) C. Postmus, J. R. Ferraro, and W. Wozniak, *Inorg. Chem.*, **6**, 2030 (1967); b) J. Bradbury, K. P. Forest, R. H. Nuttall, and D. W. Sharp, *Spectrochim. Acta*, **23A**, 2701 (1967).

23) G. B. Deacon, J. H. S. Green, and D. J. Harrison, *ibid.*, **24A**, 1921 (1968).

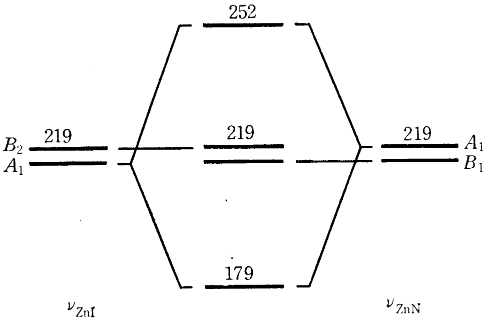

Fig. 2. Schematic illustration of the mode mixing in the 250—150 cm^{-1} region for $ZnI_2 \cdot 2CH_3CN$.

bromide. If this is the case for the present iodide, the ν_{ZnN} and ν_{ZnI} of the A_1 species would couple strongly with each other to result in a comparatively large splitting. Thus, we considered that the ν_{ZnN} and ν_{ZnI} of the A_1 species were split into bands at 252 and 179 cm^{-1}, while the B_1 and B_2 modes remained overlapped at 219 cm^{-1}, as is illustrated in Fig. 2. The band at 153 cm^{-1} for the iodide is slightly lower in position than the corresponding bands for the chloride and bromide, at 163 and 162 cm^{-1} respectively, which were assigned to δ_{NZnN}. This slight lowering in frequency for the iodide is probably due to a coupling of this bending mode with the ν_{ZnI} of the A_1 species. All the bands for $ZnI_2 \cdot 2CH_3CN$ can thus be interpreted successfully by assigning the bands near 210 cm^{-1} to the ν_{ZnN} of the chloride and bromide, and by considering the iodide to have a similar Zn–N coordinate bond. The assignments made for the skeletal modes are shown in Table 2.

Normal Coordinate Analysis

The normal coordinate analyses by the *G-F* matrix method were carried out in order to confirm these assignments and estimate the bond strength between the zinc atom and the ligand. The structure of $ZnCl_2 \cdot 2CH_3CN$ has been reported by Isakov and Zvonkova to have a distorted tetrahedral structure about the Zn atom, with a linear C–C≡N frame and specifically with a Zn–N≡C angle of 111°, a value considerably less than 180°.[17] The nonlinearity of a metal–N≡C system has been reported for the addition compounds of $CuCl_2$ and CH_3CN (∠CuNC=160°),[24] while the linearity of some metal–N≡C–C systems has been confirmed by X-ray structure analyses for nitrile complexes, such as $SnCl_5 \cdot CH_3CN$[25] and $BX_3 \cdot CH_3CN$.[26] It is probable that the metal–N≡C system is not linear in the crystalline state. However, whether or not such an angle as small as 111° is real in $ZnCl_2 \cdot 2CH_3CN$ will require further investigation. Since all the spectral evidence supports the idea that the C≡N triple bond, advantageous to forming a linear linkage, is virtually retained in the present complexes, in our calculations we did not adopt the results of the crystal structure analysis, but, rather, preferred the following assumed molecular geometry. The structure of a free nitrile as determined by microwave spectroscopy was employed for the ligands.[27] The Zn–N≡C angle was assumed to be 180°, as in previous normal coordinate analyses of nitrile complexes,[6,7,13] and the other valency angles about the Zn atom were assumed to be tetrahedral angles, 109.5°. The Zn–N distance was assumed to be 2.00 Å, and the Zn–X distances, to be 2.30, 2.38, and 2.48 Å for Cl, Br, and I respectively, referring to the literature on several zinc halide complexes.[16]

The complexes are expected to undergo thirty-nine normal modes of vibration, $13A_1+7A_2+11B_1+8B_2$, among which the two torsional vibrations of the methyl groups, A_2+B_2, were not treated because the torsional force constant could be considered to be nearly zero.

A force field of the modified Urey-Bradley type was used:

$$2V = \sum_{ij} K_{ij}(\varDelta r_{ij})^2 + \sum_{ij} H_{ij} r_i^0 r_j^0 (\varDelta \alpha_{ij})^2 + \sum_{ij} F_{ij}(\varDelta q_{ij})^2 + \sum_{ij} F'_{ij} q^0_{ij}(\varDelta q_{ij}) + \kappa(\text{methyl}) + f(\varDelta\alpha_{ZnNC} \cdot \varDelta\alpha_{NCC})$$

where κ is the force constant for the internal tension of the valence angles of the methyl group and where f is the force constant for the interaction between the Zn–N≡C bending and the C–C≡N bending. The internal tension about the Zn atom was not introduced into the force field, since the bands corresponding to the skeletal deformation modes were not observed. The force constants for the ligand were determined so as to reproduce the observed frequencies for the liquid acetonitrile listed in Table 1, by starting with the force constants of the Urey-Bradley force field determined for free acetonitrile by Nakagawa and Shimanouchi.[18] The force constants thus obtained are shown in Table 3.[28] By transferring them to the complexes, the force constants related to the skeletal modes were then determined by a brute-force method. In the calculations, the force constants, H_{XZnX}, H_{NZnX}, F_{XX}, and F_{NX}, were assumed at plausible values. Since the three complexes have nearly identical coordinate bonds identical force constants associated with the nitrogen atom were chosen for the three complexes, and they were determined so as to reproduce best the observed frequencies belonging to the B_1 species rather than

TABLE 3. FORCE CONSTANTS FOR LIQUID ACETONITRILE (in mdyn/Å)

K_{CC}	4.38	H_{CCH}	0.41	F_{CCH}	0.34
K_{CH}	4.66	H_{HCH}	0.29	F_{HCH}	0.27
K_{CN}	17.35	H_{CCN}	0.19	F_{CCN}	0.00
κ[a]	0.103				

a) κ in mdyn·Å units.

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24) R. D. Willett and R. E. Rundle, *J. Chem. Phys.*, **40**, 838 (1964).

25) H. Binas, *Z, Anorg. Chem.*, **352**, 271 (1967).

26) B. Swanson, D. G. Schriver, and J. A. Ibers, *Inorg. Chem.*, **8**, 2183 (1969).

27) C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958).

28) The normal coordinate analyses using different approximations have also been carried out by other workers.[21,29] The force constants listed in Table 3 were recalculated using the frequencies for liquid acetonitrile observed by us and accordingly, slightly different from those obtained by Nakagawa and Shimanouchi.

29) J. L. Duncan, *Spectrochim. Acta*, **20**, 1197 (1964).

Table 4. Force constants for $ZnX_2 \cdot 2CH_3CN$ (in mdyn/Å)[a]

K_{ZnN}		0.56	
H_{NZnN}		0.057	
H_{ZnNC}		0.065	
F_{NN}		0.084	
F_{ZnC}		0.000	
f[b]		0.037	
	X=Cl	X=Br	X=I
K_{ZnX}	1.10	1.10	0.89
H_{XZnX}	(0.075)	(0.035)	(0.035)
H_{NZnX}	(0.023)	(0.023)	(0.024)
F_{XX}	(0.075)	(0.075)	(0.075)
F_{NX}	(0.036)	(0.036)	(0.046)

a) Assumed values were parenthesized.
b) f in mdyn·Å units.

Table 5. Observed and calculated frequencies for $ZnX_2 \cdot 2CH_3CN$ complexes (in cm^{-1})[a]

Symmetry species	X=Cl		X=Br		X=I	
	obsd	calcd	obsd	calcd	obsd	calcd
A_1	398	394	396	394	395	394
	265	291	247	247	252	230
	210	192	212	177	179	176
	163	174	162	165	153	153
	—	119	—	88	—	73
	—	37	—	37	—	36
B_1	380	383	379	383	378	383
	210	210	212	210	219	215
	125	126	128	125	132	125
	—	61	—	51	—	48
B_2	389	386	386	386	385	386
	333	307	261	256	219	219
	125	144	128	138	132	133
	—	43	—	37	—	34

those belonging to the other species, for the B_1 modes were considered to have no appreciable mode mixings with one another. Among the Zn–X force constants, the K_{ZnI} was determined by using mainly the observed frequencies belonging to the B_2 species in order to see clearly the influence of the mode mixing in the A_1 species. The resulting force constants of the skeleton are listed in Table 4. Table 5 compares the observed and calculated frequencies in the low-frequency region. The non-zero force constant, $f(\Delta\alpha_{ZnNC} \cdot \Delta\alpha_{NCC})$, had to be used in order to obtain calculated C–C≡N bending frequencies in agreement with the observed ones. By introducing this interaction term, the splitting into three bands and the high-frequency shift by about 30 cm^{-1} observed for the δ_{CCN} were accounted for satisfactorily. It must be noted that the calculated Zn–N≡C bending frequencies of the A_1 species were not brought into a frequency region higher than 70 cm^{-1} even if such a cross term was taken into consideration. The spectra in the Zn–I and Zn–N stretching frequency region were previously explained qualitatively in the section of the assignments. This now becomes clearer, as may be seen in Table 5; that is, Table 5 justifies the interpretation that the specific features in the spectra of the iodide are caused by the mode mixings, which were enhanced by the lowering of the Zn–X stretching frequency due mainly to an increase in the mass of the halogen atom. However, since the potential energy distribution for the bands at 252 and 179 cm^{-1} is changed delicately by a slight change in the force constants, the dominant contributor to each band can not be specified definitely. If the Zn–N≡C system is nonlinear, then some force constants necessarily change from the values listed in Table 4. However, it was assured by normal coordinate treatments for bent systems that the K_{ZnN} was substantially unchanged unless the Zn–N≡C angle was extremely small, such as below 150°.

It seems necessary here to comment on the high frequency shifts of the C≡N and C–C stretching frequencies upon coordination. The calculated frequencies for the ν_{CC} were 934 cm^{-1} for the A_1 species and 930 cm^{-1} for the B_2 species. This indicates that a fairly large high-frequency shift occurs in complexing without altering the K_{CC} value. In contrast, the high-frequency shift of the ν_{CN} cannot be explained without assuming an increase in the K_{CN} value, as has been pointed out previously.[1,20] If one wishes a better agreement with the observed frequencies, 2273, 2285, and 2274 cm^{-1} for the chloride, bromide, and iodide respectively, the K_{CN} values must be increased by 0.30, 0.42, and 0.30 mdyn/Å respectively.

Zn–N Force Constant

Table 6 shows the observed frequencies related to the Zn–N stretching mode for several complexes of zinc halides with ligands containing nitrogen as a donor atom. It can be seen in Table 6 that, while the bands for the amine complexes are located at 500—400 cm^{-1}, those for the imine and nitrile complexes lie in a much lower frequency region, 250—200 cm^{-1}. In order to show the strength of the coordinate bonds, Table 7 shows the K_{ZnN} values for $ZnX_2 \cdot 2NH_3$,[30,31] $ZnX_2 \cdot 2CH_3CN$ and $ZnX_2 \cdot 2$ (imidazole),[32] which represent the three types of coordination. The Zn–N force constants for all the complexes listed in Table 6 were not available, and we did not try complete normal coordinate analyses for all these complexes. However, the K_{ZnN}'s in pyridine and thiazole complexes, which have ring systems similar to imidazole, may be considered to have the same order of magnitude as that for the imidazole complexes. The relatively low frequency for the imidazole complex results from the mass effect of the imidazole ring. Thus, the K_{ZnN} values for the nitrile complexes can be said to be much smaller than those for the amine and imine complexes. Ozin

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[30] K. Krishnan and R. A. Plane, *Inorg. Chem.*, **5**, 852 (1966).

[31] T. Kamo, H. Shibuya, and M. Kimura, unpublished work. The force constants for $ZnX_2 \cdot 2NH_3$ were derived by Krishnan and Plane by means of a five-body approximation.[30] The present authors also observed the spectra of $ZnCl_2 \cdot 2NH_3$, calculated the force constants by solving an eleven-body problem, and were led to the same result as that reported by Krishnan and Plane.

[32] C. Perchard and A. Novak, *Spectrochim. Acta*, **26A**, 871 (1970).

[33] J. A. Weaver, P. Hambright, P. T. Talbert, E. Kang, and A. N. Thorpe, *Inorg. Chem.*, **9**, 268 (1970).

TABLE 6. OBSERVED Zn–N STRETCHING FREQUENCIES OF SOME ZINC HALIDE COMPLEXES WITH *N*-DONORS (in cm^{-1})

	X=Cl	X=Br	X=I
$ZnX_2(NH_3)_2$[a]	432, 429	428, 421	412, 404
$ZnX_2(NH_2CH_2CH_2NH_2)$[b]	480, 468 405	—	—
$ZnX_2(Py)_2$[c]	218	219	222
$ZnX_2(ImH)_2$[a]	259, 244	266, 248	267, 240
$ZnX_2(4\text{-MeT})_2$[b]	239	240, 239	274
$ZnX_2(CH_3CN)_2$[e]	210	212	219

a) ImH: imidazole; Ref. 32.
b) Ref. 30.
c) Py: Pyridine; this molecule was studied by Postmus *et al.*, Ref. 22a, and by Bradbury *et al.*, Ref. 22b. The values listed in Table were quoted from the former atuhors' results.
d) 4-Methyl thiazol; Ref. 33.
e) Present work; for the iodide the frequencies assigned to the B_1 species was entered, see text.

TABLE 7. STRETCHING FORCE CONSTANTS, K_{ZnN} FOR THE COMPLEXES WITH *N*-DONORS IN DIFFERENT VALENCY STATES (in mdyn/Å)

	X=Cl	X=Br	X=I
$ZnX_2\cdot(NH_3)_2$[a]	1.42	1.38	1.28
$ZnX_2\cdot(ImH)_2$[b]	1.21	1.21	1.21
$ZnX_2\cdot(CH_3CN)_2$[c]	0.65	0.65	0.65

a) Refs. 30 and 31.
b) Ref. 32.
c) present work.

and Walton have found that a value of 0.4 mdyn/Å is best for the metal-nitrogen stretching force constants of the 1:1 complexes of $NbCl_5$ and $TaCl_5$ with acetonitrile.[7] This value is of about the same order as that obtained by us. Pd(II) and Pt(II) halide-acetonitrile complexes must also have a similar force constant in view of their low stretching frequencies as suggested by Walton.[9] On the other hand, much larger force constants, 2.5—3.5 mdyn/Å for $BX_3\cdot CH_3CN$ molecules and 2.0—3.0 mdyn/Å for $XCN\cdot AlCl_3$, have been reported by Shriver and Swanson[11] and by Kawai and Kanesaka[13] respectively. On surveying these data, it may be noted that the coordinate bonds of ordinary metal halide-alkyl cyanide complexes have force constants of 0.6—0.4 mdyn/Å, giving rise to absorption bands around 200 cm^{-1}, unless some other causes for strengthening the M–N bonds are present. It seems that the strength of the M–N coordinate bond is dependent largely on the valency state or the hybridized state of the nitrogen atom, but is independent of the substituents, and that the order is $sp^3 \geq sp^2 > sp$. Furthermore, the approximate force constants and stretching frequencies of Zn–N coordinate bonds may be predicted from the valency state of the nitrogen atom involved.

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